

TITLE OF THE INVENTION

PROCESS FOR PRODUCING METAL FOIL

BACKGROUND OF THE INVENTION

5 The present invention relates to a process for producing metal foil, and more particularly to a process for continuously producing metal foil by electrodepositing copper, nickel or like metal foil on a rotating cylindrical cathode and thereafter peeling the foil off, the process using an auxiliary anode in
10 addition to the main anode for adjusting the current density when starting the electrodeposition so as to produce foil having a uniform quality and free from pinhole defects.

FIG. 2 shows a typical process for producing metal foil, i.e., a conventional process wherein an electrolytic reaction
15 is conducted for producing copper foil for use in printed circuit boards or the like. The process uses an electrolytic vessel provided with a cylindrical cathode 1 rotatable in the direction of an arrow A, and an anode 2 having a curved surface opposed to the cathode. An electrolytic solution is forced against
20 and supplied to the cathode from a slit 4 in the central lower portion of the anode and is thereby passed through a clearance 5 between the cathode and the anode to conduct electrolysis and electrodeposit metallic copper foil of predetermined thickness on the surface of the cathode. The copper foil is peeled off
25 and wound up by a winder 6 for continuous production.

The anode for use in such an electrolytic bath is conventionally made from lead or lead alloy, whereas lead has

the problem of becoming consumed relatively rapidly to contaminate the electrolytic solution and degrade the product with dissolved lead. Accordingly, various insoluble anodes are proposed recently which comprise an anode material and an
5 electrode-active coating layer formed on the material and containing a noble metal oxide.

Although the problem of contaminating the electrolytic solution and degrading the product has been ameliorated to some extent by the use of this type of insoluble anode, it is required
10 to provide copper foil of ever decreased thickness with an increase in the complexity of printed circuit boards in recent years. Production of thinner copper foil increases the possibility of developing pinhole defects, so that various means have been proposed for controlling the current density for the
15 initial stage of electrodeposition by providing an auxiliary anode in addition to the main foil producing anode [e.g., JP-A No. 10-18076(1998)].

When the auxiliary anode is to be used in existing copper foil production apparatus, the location where this anode is to
20 be installed is greatly limited, with the result that the insoluble anode becomes inoperative for electrolysis or locally inactivated within a short period of time, for example, because of a relatively small electrode area and a relatively high current density. When a conventional insoluble electrode is
25 used as an auxiliary anode, it becomes electrolytically inoperative within a short period of time. Therefore it is frequently replaced, because local inactivation results in

uneven deposition on the cathode, leading to the production of faulty product. The use of the expensive noble metal as an electrode active substance for conventional auxiliary anode is not advantageous economically.

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SUMMARY OF THE INVENTION

It is required that the auxiliary anode of the copper foil production apparatus should be operated with a pulse current or at a high current density of at least 50 A/dm^2 in view of the purpose of use. The conventional electrode containing a platinum group metal oxide becomes electrolytically inoperative or locally inactivated within a short period of time if operated under such a condition. We have conducted extensive research in an attempt to overcome this problem and found that an auxiliary anode having a tantalum intermediate layer formed between a titanium substrate and a coating layer of an electrode active substance containing a platinum group metal oxide is exceedingly superior in function and durability to electrodes comprising a titanium substrate and the same coating layer as above formed directly on the substrate. Thus the present invention has been accomplished.

In producing metal foil by passing an electric current between a cylindrical cathode immersed in an electrolytic solution and an anode opposed to the cathode, continuously electrodepositing a metal layer on a surface of the cathode while rotating the cathode and thereafter peeling the metal layer off, the present invention provides a process for producing metal

foil characterized in that an auxiliary anode capable of adjusting the current density when electrodeposition is started is disposed at one side of the cathode where an unelectrolyzed portion thereof is brought into the electrolytic solution, at
5 a position downstream from the anode with respect to the direction of flow of the electrolytic solution, the auxiliary anode being an electrode having a coating layer comprising an electrode active substance containing a platinum group metal or a platinum group metal oxide, or a mixture of an oxide of a valve metal and a platinum group metal or a platinum group metal oxide and
10 formed over an electrically conductive metal substrate comprising titanium or a titanium alloy, with an intermediate layer of tantalum or a tantalum alloy formed between the coating layer and the substrate.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a view in vertical longitudinal section schematically showing an embodiment including an auxiliary anode; and

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FIG. 2 is a view in vertical longitudinal section schematically showing a conventional apparatus for electrolytically producing copper foil.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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The auxiliary anode for use in the present invention has an electrically conductive metal substrate which is made from metallic titanium or a titanium alloy such as titanium-tantalum,

titanium-tantalum-niobium, titanium-palladium or the like. The substrate may be in the form of a plate, perforated plate, bar or net, or in any desired form.

The auxiliary anode has an intermediate layer which is provided by a thin film of tantalum or a tantalum alloy. The thin film can be formed by sputtering, ion plating or vacuum evaporation. The tantalum alloy is preferably tantalum-niobium, tantalum-titanium or like alloy. The sputtering processes usable are high-frequency sputtering and d.c. bipolar sputtering. Such a process is preferably magnetron sputtering. The thin film serving as the intermediate layer is preferably 1 to 10 μm , more preferably 1 to 7 μm , most preferably 1 to 5 μm , in thickness. When too thin, the thin film will not be formed satisfactory on the substrate, whereas excessive thicknesses result in problems such as difficulty encountered in sputtering. Stated more specifically, a high-frequency discharge is effected in an argon gas atmosphere having a high vacuum of less than 1×10^{-2} torr. The distance between the substrate and the target is suitably determined, for example, from the range of 10 to 80 mm. The temperature of the substrate is suitably determined, for example, from the range of 150 to 230° C. It is further desired to fully remove the remaining gas. The sputtering operation is conducted for a suitably selected period, for example, from 30 to 200 minutes, whereby a tantalum or tantalum alloy thin film of desired thickness is formed on the substrate.

A coating layer (catalyst layer) comprising an electrode active substance having electrochemical activity is formed on

the intermediate layer thus formed and having no electrode activity. The electrode active substance suitable for electrodes involving evolution of oxygen comprises (or contains) a platinum group metal or platinum group metal oxide, or a mixture of a platinum group metal or platinum group metal oxide and an oxide of a valve metal such as titanium, tantalum, niobium, zirconium or the like. Typical examples of electrode active substances comprises (or contains) a mixture of iridium oxide and tantalum oxide, mixture of iridium oxide and titanium oxide, mixture of iridium oxide and ruthenium oxide, mixture of iridium oxide, ruthenium oxide and titanium oxide, mixture of ruthenium oxide and titanium oxide, or mixture of ruthenium oxide and tantalum oxide. The electrode active substance which is especially preferable is one having high durability and comprising (or containing) a mixture of 60 to 95 wt. %, preferably 70 to 95 wt. %, of iridium oxide calculated as metallic iridium and 5 to 40 wt. %, preferably 5 to 30 wt. %, of tantalum oxide calculated as metallic tantalum.

The coating layer comprising an electrode active substance can be formed by a process conventionally used, such as thermal decomposition, electrochemical oxidation or powder sintering. The thermal decomposition process is especially desirable. More specifically, a solution of such metallic salts is applied to the surface of the intermediate layer several times and dried, eventually followed by a heat-treatment at 350 to 550° C. The thickness of the coating layer is determined suitably, for example, from the range of 1 to 50 μ m.

The anode, i.e. the main anode may be made, for example, from lead or a lead alloy. The anode may be an insoluble electrode comprising an anode material and a coating layer comprising an electrode active substance. The electrode active substance for the main anode may be suitably selected from among those mentioned above for the auxiliary anode.

The cathode may be made from chromium, titanium or the like. Since the cathode prepared from such a material has a stable oxide film over the surface, the metallic copper film formed by electrodeposition is unlikely to adhere to the underlying cathode surface with a high strength and can therefore be peeled off from the surface as a thin metallic film.

The electrolytic solution and the electrolysis conditions may be those usually used for forming copper, nickel or like metal foil by electrodeposition.

The metal foil production apparatus shown in FIG. 1 has an electrolysis vessel which is internally provided with a cylindrical cathode 1 rotatable in the direction of an arrow A, and an anode 2 having a curved surface opposed to the cathode. In the electrolysis vessel, an electrolytic solution is forced against and supplied to the cathode from a slit 4 in the central lower portion of the anode and is thereby passed through a clearance 5 between the cathode and the anode. Electric current is passed between the cathode 1 and the anode 2 to conduct electrolysis and electrodeposit metallic copper foil of predetermined thickness on the surface of the cathode. The copper foil is peeled off and wound up by a winder 6 for continuous

production. The portion of the electrolytic solution flowing through the clearance 5 egresses from an outlet 9 of the clearance 5 and returns to the interior of the vessel.

The auxiliary anode 7 for adjusting the current density is installed as opposed to a position 8 where the unelectrolyzed portion of the cathode immersed in the electrolytic solution comes into contact with the portion of the solution flowing out of the outlet 9 of the clearance 5 between the cathode 1 and the anode 2 and a weak electric current starts to flow. Usually, this position of installation is slightly downstream from the outlet 9 with respect to the direction of flow of the electrolytic solution. The auxiliary anode 7 in the form of a flat plate is disposed horizontally. The anode 7 is positioned in proximity to the cathode 1, with the solution prevented from reaching the upper surface of the anode 7. In the case where the cylindrical cathode 1 is 100 mm in diameter and 100 mm in width, with the flat platelike auxiliary anode 7 measuring 100 mm \times 5 mm \times 1.5 mm, the distance between the cathode 1 and the auxiliary anode 7 is suitably determined, for example, from the range of 0.3 to 5 mm. The surface of the auxiliary anode 7 opposed to the cathode 1 has an area sufficient to pass electric current therethrough until particles are uniformly initially deposited on the cathode and grown thereon. The current to be passed from the auxiliary anode 7 to the cathode 1 has such a magnitude as to give a current density sufficient to produce nuclei uniformly on the cathode surface over an area thereof opposed to the auxiliary anode 7. If the current density is increased markedly

to a predetermined value by the auxiliary anode 7 in this way at the time a weak current starts to flow, with the cathode 1 coming into contact with the electrolytic solution when electrodeposition is started, over-potential is available which is sufficient to produce deposited particles anew over the entire cathode surface. Consequently, the formation of nuclei with the start of uniform electrodeposition and growth of particles initially deposited can be effected over the entire surface without being influenced by the uneven underlying surface state of the cathode. Thus, the provision of the auxiliary anode obviates uneven formation of nuclei with the start of electrodeposition and uneven growth of initially deposited particle that would otherwise occur, precluding occurrence of pinholes in the foil due to an uneven distribution of thicknesses owing to these drawbacks and making it possible to produce a thin metal foil product of uniform thickness.

The current density is adjusted as described above by using as the auxiliary anode an electrode having a coating layer of electrode active substance formed over a conductive metal substrate with an intermediate layer interposed therebetween to thereby eliminate the rise in the voltage and local inactivation of the electrode over a long period of time, consequently making it possible to produce metal foil of uniform thickness with good stability.

The process of the invention is usable also for producing nickel or other metal foil, other than copper foil, by an electrolytic reaction.

EXAMPLES

The present invention will be described below in greater detail with reference to examples and comparative examples.

5 Example 1

The metal foil production apparatus shown in FIG. 1 has an electrolysis vessel, which is internally provided with a cylindrical cathode 1 measuring 100 mm in diameter and 100 mm in width and rotatable in the direction of an arrow A, and an
10 anode 2 having a curved surface opposed to the cathode. An auxiliary anode 7 in the form of a flat plate measuring 100 mm \times 5 mm \times 1.5 mm for adjusting the initial current density is disposed horizontally in the electrolysis vessel at one side of the cathode 1 where the cathode in rotation is brought into
15 an electrolytic solution.

The auxiliary anode 7 was prepared in the following manner. First, the electrode surface of a titanium plate for the substrate of the auxiliary anode was degreased by ultrasonic cleaning, and the titanium plate was thereafter blasted over both surfaces
20 thereof with #30 alundum under a pressure of 4 kgf/cm² for about 10 minutes. The titanium plate thus treated was washed in running water overnight and dried.

The electrode substrate thus obtained was placed into a high-frequency magnetron apparatus. At this time, a tantalum
25 target, 300 mm in diameter and 3 mm in thickness, was spaced apart from the substrate by a distance of 40 mm, and the chamber was adjusted to an internal pressure of less than 1×10^{-6} torr.

Argon gas was introduced into the chamber to an internal pressure of 1×10^{-2} torr. A high-frequency sputtering operation was then conducted at 13.56 MHz for about 60 minutes. At this time, the high-frequency power applied was 200 W (0.3 kV), and the substrate temperature was 170° C. This operation formed a tantalum thin film (intermediate layer) having a thickness of about 2 μ m and weighing about 30 g/m² on the electrode substrate. The surface of the thin film obtained was analyzed by the X-ray diffraction method (XRD), which revealed a diffraction pattern of beta-tantalum.

The following ingredients for an electrode active substance coating composition was applied to the tantalum thin film on the electrode substrate.

	TaCl ₅	0.32 g
15	H ₂ IrCl ₆ •6H ₂ O	1.00 g
	35% HCl	1.0 ml
	n-CH ₃ (CH ₂) ₃ OH	10.0 ml

The coated substrate was dried at 100° C for 10 minutes and then baked in an electric furnace at 500° C for 20 minutes. This coating procedure to prepare the active substance was repeated five times to form a coating layer comprising iridium oxide serving as an electrode active substance (composition ratio by weight of the coating layer calculated as metals: Ir/Ta = 7/3).

With reference to FIG. 1, the electrode thus prepared was used as the auxiliary anode in the copper foil production apparatus, as opposed to the cathode 1 at a predetermined distance

therefrom. The auxiliary anode was disposed on one side of the rotating cathode 1 where the unelectrolyzed portion thereof was brought into the electrolytic solution, at a position slightly downstream (with respect to the direction of flow of the solution) from the outlet 9 of the clearance 5 between the cathode 1 and the anode 2, more specifically at a position where the unelectrolyzed portion in the solution came into contact with the portion of the solution flowing out of the outlet 9 of the clearance 5, and a weak current started to flow. The distance between the cathode 1 and the auxiliary anode 7 was 2 mm.

The cathode 1 was made from chromium. The anode 2 was made from a lead alloy.

An aqueous solution containing 100 g/L of sulfuric acid, 250 g/L of copper sulfate and a glue serving as an additive was prepared as the electrolytic solution, and the solution was supplied to the electrolysis vessel so as to cause the solution to flow along the cathode surface at a rate of 2 m/sec. The cathode 1 was rotated while passing current between the cathode 1 and the anode 2 at a current density of 120 A/dm^2 and passing current through the auxiliary anode 7 at 200 A/dm^2 . The electrolytic solution was forced out against and supplied to the cathode from a slit 4 in the central lower portion of the anode 2 to pass the solution through the clearance 5 between the cathode 1 and the anode 2 for electrolysis and electrodeposit metallic copper foil, $35 \text{ }\mu\text{m}$ in thickness, on the cathode surface. The foil was peeled off the cathode and wound up by a winder 6. The portion of the solution flowing through the clearance

5 egressed from the outlet 9 and was returned to the interior of the electrolysis vessel. The time taken for the electrolysis starting voltage of the auxiliary anode 7 to increase by 3 V from the initial value was taken as the electrode life. After
 5 conducting electrolysis for 100 hours, the foil was checked for thickness along the width thereof at an interval of 1 cm using a film thickness meter. Table 1 shows the result of measurement of foil thickness and the life of the auxiliary anode.

Example 2

10 A titanium plate treated in the same manner as in Example 1 was positioned at a distance of 20 mm from a tantalum target and subjected to a tantalum sputtering operation. The thin film obtained was checked by XRD, which revealed a diffraction pattern of alpha-tantalum. An auxiliary anode was prepared by forming
 15 a coating layer of electrode active substance on the surface of the thin film by the same procedure as in Example 1. The electrode was tested in the same manner as in Example 1 for electrolytically producing foil. Table 1 shows the result of measurement of the foil thickness and the life of the auxiliary
 20 anode. The same other procedures as in Example 1 were repeated.

Example 3

An auxiliary anode having a beta-tantalum intermediate layer was fabricated in the same manner as in Example 1 with the exception of using the following coating composition.

25	TaCl ₅	0.18 g
	H ₂ IrCl ₆ •6H ₂ O	1.00 g
	35%HCl	1.0 ml

n-CH₃(CH₂)₃OH 10.0 ml

The electrode was tested in the same manner as in Example 1 for electrolytically producing foil. Table 1 shows the result of measurement of the foil thickness and the life of the auxiliary
5 anode.

Example 4

A titanium plate treated in the same manner as in Example 1 was maintained at 50° C by cooling, positioned at a distance of 40 mm from a tantalum target and subjected to a tantalum
10 sputtering operation in the same manner as in Example 1. When checked by XRD, the thin film obtained was found to contain tantalum of amorphous structure. An auxiliary anode was fabricated by forming a coating layer of electrode active substance on the surface of the thin film by the same procedure
15 as in Example 1. The electrode was tested in the same manner as in Example 1 for electrolytically producing foil. Table 1 shows the result of measurement of the foil thickness and the life of the auxiliary anode.

Example 5

20 A titanium plate treated in the same manner as in Example 1 was placed into an ion plating apparatus and subjected to an ion plating operation using a tantalum vacuum evaporation source to obtain a tantalum ion-plating layer (intermediate layer) having a thickness of 5 μm. An auxiliary anode was fabricated
25 by forming a coating layer of electrode active substance on the surface of this layer by the same procedure as in Example 1. The electrode was tested in the same manner as in Example 1 for

electrolytically producing foil. Table 1 shows the result of measurement of the foil thickness and the life of the auxiliary anode.

Comparative Example 1

5 The same electrode coating composition as used in Example 1 was applied directly to the surface of a titanium plate treated in the same manner as in Example 1 to similarly form a coating layer wherein iridium oxide served as an electrode active substance and to fabricate an auxiliary anode. The electrode
10 was tested in the same manner as in Example 1 for electrolytically producing foil. Table 1 shows the result of measurement of the foil thickness and the life of the auxiliary anode.

Example 6

15 The same auxiliary anode as used in Example 1 was tested for electrolytically producing foil by the same procedure as in Example 1 except that a pulse current was used as the current. The pulse electrolysis conditions were a current density of 200 A/dm², pulse electrolysis time of 10 milliseconds and cessation time of 10 milliseconds. The time taken for the electrolysis
20 starting voltage of the auxiliary anode to increase by 3 V from the initial value was taken as the electrode life. Table 2 shows the life of the auxiliary anode.

Comparative Example 2

25 The same auxiliary anode as used in Comparative Example 1 was used under the same conditions as in Example 6 for a pulse electrolysis test. Table 2 shows the result.

Table 1

	Thickness of Ta intermediate layer μm	Uniformity of foil thickness 100 hrs later	Electrode life (hours)	
5	Example 1	2	Good	1150
	Example 2	2	Good	1040
10	Example 3	2	Good	1190
	Example 4	2	Good	1100
	Example 5	5	Good	970
15	Comp. Ex. 1	0	Poor	460

Table 2

		Thickness of Ta intermediate layer <u>μm</u>	Electrode life <u>(hours)</u>
25	Example 6	2	870
	Comp. Ex. 2	0	240

30 The foregoing results of Examples and Comparative Examples reveal that the use of the auxiliary anode having an intermediate layer of tantalum results in an electrode life twice as long as that provided by an auxiliary anode having no intermediate layer, further producing foil of uniform thickness and

35 satisfactory quality without permitting local separation of the coating layer, i.e., the catalyst layer.

 The auxiliary anode for use in the present invention comprises a conductive metal substrate of titanium or an alloy thereof, and a coating layer of electrode active substance formed

40 over the substrate, with an intermediate layer of tantalum or an alloy thereof interposed therebetween. The intermediate layer prevents electrolytic oxidation of the substrate of

titanium or alloy thereof and itself has corrosion resistance, resistance to electrolytic oxidation and satisfactory electrical conductivity. These characteristics are useful for pulse electrolysis. Furthermore, the coating layer comprising
5 an electrode active substance and formed on the intermediate layer retains good adhesion to the intermediate layer, has high catalytic activity and remains highly durable against local inactivation over a prolonged period of time. The auxiliary anode having the intermediate layer is exceedingly superior in
10 these characteristics to the auxiliary anode having no intermediate layer.